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Project Summary

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Evaluation of Methods for Hazardous Chemicals Listed in Appendix D to 40 CFR 122 (Table V)

S. V. Lucas, M. Cooke, and T. F. Cole

This study involved method development for several compounds that had not been tested by existing U.S. EPA Methods: semivolatiles volatiles (6 compounds), purgeables (3 compounds), volatile amines (6 compounds), and alcohol amines (2 compounds). These compounds are on a list of 75 organic compounds in Table V of Appendix D to 40 CFR 122. Of those 75 compounds, 24 had not been tested by an existing EPA method for analysis in water and wastewater. The present work reports on efforts to demonstrate the analytical performance of 17 of those 24 compounds plus an additional five compounds not included in Table V of Appendix D by applying existing 600-series methods with appropriate modifications. In each case, a test analyte set for a given method/approach consisted of essentially all of the Appendix D Table V compounds belonging to that compound class. The approach was to demonstrate performance separately in the areas: (1) chromatography -using fused silica capillary columns whenever possible and including the evaluation of cold, on-column injection whenever necessary, (2) modified extraction and concentration techniques, and (3) modified cleanup techniques. In cases where all of these areas gave appropriate results, an integrated method was tested for accuracy and precision.

For the semivolatile compounds (6 of the 17), two compounds (benzonitrile and quinoline) gave excellent recovery and precision through extraction and cleanup, three other compounds (kepone, strychnine and dichlone) gave 50 to 80 percent recovery, and one compound (trichlorfon) was not stable in aqueous systems at neutral pH.

For the purgeable compounds (3 of 17), one analyte (propylene oxide) gave marginally acceptable precision results, with the observed deficiency apparently due to hydrolysis during the purge-and-trap desorption step. The other two analytes gave unacceptable results but for different reasons: allyl alcohol was purged with efficiency only 15 percent at 85°C and also gave unacceptable GC peak tailing, resulting in a relatively high estimated detection limit of 70 µg/L. Although methyl mercaptan also exhibited some tendency toward decomposition on the trap, the principal difficulty is its elution early in the chromatogram where baseline disturbances and methanol elution occur. A "Hall detector" in the sulfur detection mode is recommended for analysis of methyl mercaptan by the room temperature purge-trap-desorb approach.

For the volatile amines (6 of the 17), a special GC packing material was prepared and demonstrated to be effective. However, all efforts to develop a purge-trap-desorb sample workup procedure were unsuccessful. For the alcohol amines (2 of the 17), none of the gas chromatography approaches tried provided performance adequate to justify further method development.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati,

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OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The objective of this research was to evaluate analytical methods for hazardous chemicals listed in Appendix D to 40 CFR 122 (Table V). This listing contains 75 organic chemicals that must be analyzed if they are expected to be present in existing discharges. Standard analytical methods have been developed and validated by the EPA for most of these 75 Appendix D/Table V compounds. The 24 untested compounds are listed in Table 1. Seven of these 24 untested compounds were of chemical classes that were beyond the scope of this work, and, therefore they were eliminated by the Project Officer from method evaluation. Thus, the work reported here focused on 17 of the untested compounds thought to be amenable to gas chromatography (GC). A major objective of this work was to provide a minimum number of methods to cover a maximum number of Appendix D/Table V compounds. This would minimize the effort required by the analyst. Accordingly, the Appendix D/Table V chemicals were divided into six chemical classes, each of which contained at least one of the untested compounds. These chemical classes were: organophosphorous compounds, neutral nitrogen compounds, chlorinated pesticides, extractable semivolatile bases, volatile compounds, volatile amines, and alcohol amines. The chemical class of each untested compound is identified in Table 1. In this work, methods were evaluated for all or nearly all of the Appendix D/Table V compounds of each class to ensure that method modifications which enhanced performance for a high-interest analyte did not detract from the method performance already in place for the other compounds in the class. In addition, the volatile compounds class was augmented by an additional five compounds which were not in the Appendix D/Table V listing but were of interest to the EPA Project Officer. These compounds were acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl butyl ketone, and dioxane. This report addresses a total of 22 compounds which are broadly subclassified into three sets: semivolatile (extractable) compounds, volatile (purgeable) compounds, and amines (including alcohol amines).

Experimental Design

The experimental design for each of the three compound classes incorporated independent evaluation of four aspects of a method: chromatographic separation, injection conditions, sample workup, and cleanup procedures. A main feature of the chromatographic separation evaluation for semivolatile compounds was to test both polar and nonpolar fused silica capillary columns. Injection conditions tested for the semivolatile group were evaporator cavity (split/splitless) injection at various temperatures for all compound sets and cold, on-column injection for selected compound sets. Sample workup for semivolatile compounds involved liquid-liquid extraction and extract concentration, while cleanup procedures emphasized Florisil column techniques using solvent systems already in use in EPA cleanup methods. When reasonable results were obtained in each of these areas, the precision and accuracy of the integrated method was tested.

The purge-and-trap analysis conditions were essentially those of Method 5030 employing room temperature purging with the three-component trap (Tenax, silica gel and activated carbon) for nonpolar compounds and 85°C purging with the all-Tenax trap for polar compounds. Three GC column packings were tested Porapak-QS, 10 percent Carbowax 20M on Supelcoport, and 1 percent SP1000 on Carbopack B, and the latter one was selected for the recovery and precision studies. Reagent water was used as the matrix in all spike recovery experiments, and a Tekmar LSC-2 purge-and-trap apparatus was used to generate the data.

Studies with the amine analyte set were restricted to the establishment of an adequate column packing material, feasibility studies on the purge-and-trap sample processing approach, and an investigation of the applicability of automated heated headspace sampling with capillary chromatography using a Perkin-Elmer HS-100 automated headspace sampling unit.

Results and Discussion

Organophosphorous Compounds

Trichlorfon is the only organophosphorous compound listed in Table 1, Appendix D to 40 CFR 122 (Table V) contains an additional 11 organophosphorous compounds: chlorpyriphos, coumaphos, diazinon, disulfoton, ethion, guthion, malathion, methyl parathion, mevinphos, naled, and parathion. GC studies with all 12 compounds showed that trichlorfon was essentially quantitatively decomposed upon splitless, evaporator cavity injection above 250°C. In addition, mevinphos decomposed significantly and naled decomposed slightly under those injection conditions. Therefore, cold on-column injection was used for all subsequent work. Studies using separatory funnel shakeout, reverse phase extraction, and KD concentration with the two most labile compounds (mevinphos and trichlorfon) showed that trichlorfon decomposed, essentially quantitatively, in pH 7-buffered reagent water, but that it survived KD concentration in a variety of solvents. Once it was shown that the only Table 1 organophosphorous compound, trichlorfon, was not stable in water, experimental work on the remaining 11 compounds was terminated.

Neutral Nitrogen Compounds

Of 13 neutral nitrogen compounds on the Table V list of Appendix D 40 CFR 122, benzonitrile was the only untested (Tabie 1) compound. The other 12 compounds are: diuron, dichlobenil, carbofuran, mexacarbate, carbaryl, methiocarb, and all isomers of nitrotoluene and dinitrobenzene. The chromatographic performance of all 13 compounds was tested using 30 meter SPB-5 and Carbowax 20M fused silica capillary columns. The high polarity and high molecular weight pesticides failed to elute from the Carbowax 20M column. Subsequent work with the SPB-5 column using GC-MS demonstrated that diuron decomposed quantitatively in the evaporator cavity injector at temperatures between 250 and 300°C, and that carbofuran, mexacarbate, carbaryl and methiocarb partially decomposed (up to 50 percent at 300°C) over that range. Since the untested compound benzonitrile performed well under these injection conditions, testing with cold, on-column injection was not conducted. The extraction efficiency of benzonitrile from reagent water averaged 103 ± 8 percent using methylene chloride. Extraction efficiencies for the other 12 compounds were not tested since they are all listed in current EPA methods. A Florisil column cleanup procedure was evaluated for all com-

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pounds except diuron. Nitrotoluenes were recovered in the 20 percent diethyl ether in hexane elution fraction (fraction 1). Carbofuran and carbaryl were recovered in the 15 percent acetone in hexane fraction (fraction 3). The other compounds were recovered in the 6 percent acetone in hexane fraction (fraction 2). Recoveries of all compounds were 79 percent or greater except for mexacarbate and methiocarb. They were recovered at about 35 percent. Four replicate analyses of reagent water spiked at the 25 µg/L level with the 12 compounds (diuron omitted) were carried through the extraction, concentration, and cleanup sequence. They were analyzed using a nitrogen specific detector to generate accuracy and precision data. The results showed recoveries between 72 and 80 percent with relative standard deviation (RSD) values between 10 and 15 percent for benzonitrile, and three nitrotoluenes, diclobenil and 1,2-dinitrobenzene. The recoveries for 1,3-dinitrobenzene and 1,4-dinitrobenzene were 72 ± 23 and 64 ± 12 percent, respectively. The recovery and precision data obtained for carbofuran, mexacarbate, carbaryl and methiocarb were 120 ± 17, 98 ± 25, 144 ± 20 and 10 ± 7, respectively. Undoubtedly, the observed splitless injection decomposition for these four pesticides accounts for a large measure of the variability in these results. The low (10 percent) recovery of methiocarb could not be attributed to a specific cause.

In summary, benzonitrile can be determined using methylene chloride extraction, Florisil column cleanup, and fused silica, capillary column GC analysis with nitrogen-specific detection. The overall recoveries obtained for the nitrotoluenes, dinitrobenzenes and dichlobenil were generally acceptable at 70 to 80 percent, but somewhat erratic results for carbofuran, mexacarbate, carbaryl and methiocarb prevent making any definitive method performance conclusions on those four compounds.

Chlorinated Pesticides

The two untested Table 1 compounds in this group were diclone and kepone. Methoxychlor and captan, which are also in Table V of Appendix D/40 CFR 122, were also included in the study. Of the four compounds, only diclone eluted from the Carbowax 20M fused silica capillary column. Excellent chromatographic performance was obtained for all four compounds using the SPB-5 nonpolar fused silica capillary column. Captan, however, apparently decomposed in the 300°C evaporator cavity, splitless injector. Since captan was not a high-priority, Table 1 analyte, and since this partial decomposition did not seem to have any effect on analysis precision, cold, on-column injection was not tested for this analyte set.

Neutral pH extraction of aqueous spiked samples with methylene chloride was shown to be an effective extraction approach with recovery ranging from 76 to 92 percent and precision ranging from 7 to 12% RSD. The elution scheme using Florisil column cleanup was modified by the addition of 100 percent ethyl ether and 6 percent acetone in ethyl ether elutions to provide recoveries of the four analytes.

The integrated method including methylene chloride extraction, KD concentration, Florisil column cleanup and GC-ECD analysis using a nonpolar fused silica capillary column was tested with four 1-L reagent water replicates spiked with 25 µg of each of the four analytes. All applicable Florisil column eluates were pooled before analysis. The average percent recoveries, and standard deviations obtained were diclone, 48 ± 7 percent, captan 71 ± 13 percent, kepone 74 ± 5 percent, and methoxychlor 92 ± 7 percent. The poor recovery for diclone is probably due to losses at the Florisil column cleanup step and/or KD distillation of the ethyl ether-containing Florisil elution solvent. Except for dichlone, which is an untested Table 1 compound, analysis method performance for the chlorinated pesticides was judged acceptable.

Table 1. *Untested Compounds from Table V of Appendix D to 40 CFR 122*

Compound	*Chemical Class*
Allyl alcohol	*Volatile compound*
Benzonitrile	*Neutral nitrogen compound*
Butylamine	*Amine*
Dichlone	*Chlorinated pesticide*
2,2-Dichloropropionic acid	*(Eliminated)*
Diethylamine	*Amine*
Diquat	*(Eliminated)*
Ethanolamine	*Amine*
Isopropanolamine	*Amine*
Kepone	*Chlorinated pesticide*
Methyl mercaptan	*Volatile compound*
Ethylamine	*Amine*
Methylamine	*Amine*
Naphthenic acid	*(Eliminated)*
Phenol sulfonate	*(Eliminated)*
Phosgene	*(Eliminated)*
Propargite	*(Eliminated)*
Propylene oxide	*Volatile compound*
Pyrethrins	*(Eliminated)*
Quinoline	*Extractable semivolatile base*
Strychnine	*Extractable semivolatile base*
Trichlorfon	*Organophosphorous compound*
Trimethylamine	*Amine*
Triethylamine	*Amine*

Extractable Semivolatile Bases

This group of three compounds consisted of two high-interest compounds from Table 1 (quinoline and strychnine) plus aniline. Since strychnine did not elute from the polar, Carbowax 20M column the SPB-5 (Supelco) nonpolar fused silica capillary column was used for all of the studies performed on this group. Aqueous extraction studies with methylene chloride at both neutral and basic pH, both with and without acidic pre-extraction and/or salting out (sodium chloride at 200 g/L), gave quantitative recovery of aniline and quinoline but only 46 to 58 percent recovery of strychnine. Extraction using two solvent systems, 15 percent hexane in methylene chloride, and methyl t-butyl ether, gave similar results except that the strychnine recoveries were 38 and 10 percent, respectively. A check of the KD concentration procedure indicated that for methylene chloride, the poor strychnine extraction recovery was probably due to losses at that stage. Similar results were obtained for diethyl ether, but essentially quantitative KD concentration recovery was obtained for strychnine with methyl t-butyl ether solvent. Quantitative recovery through

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the K-D step was also obtained for aniline and quinoline with both solvents. Since suitable extraction conditions could not be identified for strychnine, further work to test cleanup procedures and an integrated method for the extractable semivolatile bases was not conducted.

Volatile Compounds

Of 17 volatile compounds tested, only three are high-interest, Table 1 compounds: methyl mercaptan, propylene oxide and allyl alcohol. Fourteen other compounds were included in the volatile set. Of those 14 compounds, 9 compounds were from Table V of Appendix D 40 CFR 122, and 6 compounds were specified by EPA. This 17-compound analyte set was divided into polar and nonpolar sets for which an 85°C and ambient temperature, respectively, purge-trap-desorb approach was employed. These analyte sets are shown in Table 2. The traps used were those of Methods 8030 (85°C purge) and 8010 (ambient temperature purge) with the purge-trap-desorb conditions as specified in Method 5030. A Tekmar LSC-2 liquid sample concentrator interfaced to a GC with flame ionization detector was used for all sample analyses.

Three GC column packings were tested in this work: Porapak QS, 10 percent Carbowax 20M on Supelcoport 80/100, and 1 percent SP1000 on Carbopack B 60/80. The latter packing, in a 6 foot, 2 mm I.D. glass column, provided the best performance for all analytes and was used to produce the data reported here. Neither of the other two columns performed adequately for recommendation as a backup column in these analyses.

The most volatile analytes were checked for trap breakthrough. As expected, none of the nonpolar analyte broke through the Method 8010 trap at less than 1600 mL purge volume. For the polar analytes, only acetone and propylene oxide, with breakthrough volumes of 560 and 400 mL, respectively, for 1.0 µg trap loadings, approached the 300 mL purge volume of Method 5030.

Purging and desorption efficiencies were separately determined. For the nonpolar analytes, all but methyl mercaptan and propylene oxide were quantitatively purged and desorbed. Propylene oxide purged with only about 25 percent efficiency, and about two thirds of the purged amount apparently decomposed during desorption giving an overall recovery of 9 percent. For methyl mercaptan, 70 percent purging efficiency was found, but a 50 percent loss on desorption gave a 35 percent overall recovery. For the polar analytes, only the ketones approached quantitative purge/desorb recoveries (87 to 100 percent). Lower overall recoveries for the acetates was entirely attributable to desorption losses of 50, 20 and 35 percent for the vinyl, butyl and amyl acetates, respectively. Epichlorohydrin was also found to purge essentially quantitatively but experienced about 80 percent loss on desorption. The two remaining analytes, allyl alcohol and dioxane, were desorbed with about 90 percent recovery but were purged with only about 15 percent efficiency.

Replicate analyses of low-level spiked reagent water samples were performed to estimate the detection limits for all analytes except methyl mercaptan, and the results are shown in Table 2. Some analytical problems were encountered with all three of the high-interest analytes, propylene oxide, methyl mercaptan and allyl alcohol. Propylene oxide can be analyzed by either the room temperature or 85°C purge-and-trap approach. However, the propylene oxide data clearly indicate that this compound partially decomposes during trap desorption, and the result is that variable precision and accuracy might be expected without further method improvements. Indeed, most of the problems associated with the purge-and-trap analyte sets were shown to be associated with decomposition, probably by hydrolysis, during trap desorption. Two additional problems were encountered with methyl mercaptan: (1) FID sensitivity was low, as expected, and (2) near coelution with methanol, significantly reduced its reproducibility. Both of these problems could be eliminated with a sulfur-specific detector. In the case of allyl alcohol, the estimated detection limit of 70 µg/L was due partially to the very low purging efficiency (about 15 percent) at 85°C but primarily to the extreme GC peak tailing on the 1 percent SP1000/Carbopack B column.

Table 2. *Estimated Detection Limits for Volatile Analyte Sets*

Polar Compounds (85°C Purge)	Estimated Detection Limit, µg/L	Nonpolar Compounds (Room Temperature Purge)	Estimated Detection Limit, µg/L
allyl alcohol[a]	70	methyl mercaptan[a]	[b]
propylene oxide[a]	5	propylene oxide[a]	1.5
epichlorohydrin	10	allyl chloride	0.1
vinyl acetate	2	isoprene	0.1
butyl acetate	1	cyclohexane	0.1
amyl acetate	2	o-xylene	0.1
acetone[c]	4	ethyl ether[c]	0.1
methyl ethyl ketone[c]	0.3		
methyl isobutyl ketone[c]	0.3		
methyl butyl ketone[c]	0.6		
dioxane[c]	10		

[a] A high-interest, Table 1 compound. Note that propylene oxide is included in both analyte sets.
[b] Not determined, see discussion in text.
[c] Compound not listed in Table V of Appendix D to 40 CFR 122.

Volatile Amines and Alcohol Amines

Five of the six amines tested are high-interest, Table 1 compounds: trimethylamine, ethylamine, diethylamine, triethylamine, and butylamine. The sixth amine in the set was methylamine. The two alcohol amines tested were ethanolamine and isopropanolamine, also high-interest, Table 1 compounds.

Chromatographic characteristics of the amines were investigated using commercially available fused silica capillary columns, Carbowax 20M and DB-5, and column packings, Porapak QS and 1 percent SP1000/Carbopack B, plus a custom-made packing based on Carbopack B treated with KOH (0.3 percent) and then coated with 4.8 percent Carbowax 20M. The later column was the only one which gave adequate performance for all six amines.

Volatile amine sample workup studies were limited to feasibility investigations of purge-and-trap-based and heated headspace sampling approaches. None of the three traps tested performed adequately. The Method 8010 trap and an activated carbon trap prevented breakthrough but gave poor or no desorption recoveries. The Method 8030 trap gave good desorption

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recoveries but exhibited breakthrough for methylamine, ethylamine, and trimethylamine. Since an adequate trap was not available, purging efficiency studies were not performed. Automated heated headspace sampling performed well for tertiary amines but very poorly for primary amines, apparently due to adsorptive problems with metallic components of the autosampler. For the alcohol amines, none of the chromatographic approaches tested gave adequate chromatographic performance, and, without a determinative technique for these compounds, no further work was possible.

Conclusions and Recommendations

The low method development success rate for the 17 untested, Table 1 compounds tested reflects the multiplicity of their chemical characteristics which prevent analysis using ordinary approaches. Only six of the 17 untested Table 1 compounds (benzonitrile, quinoline, kepone, strychnine, dichlone and propylene oxide) gave acceptable or marginally acceptable results. One compound, trichlorfon, is not stable in water, and no further method development work for aqueous matrices should be pursued. Further method development for methyl mercaptan should include a purge-and-trap approach with Hall electrolytic conductivity/sulfur mode detection. If the chromatographic tailing problem can be solved, allyl alcohol may be effectively analyzed with an 85°C purge-and-trap approach even though it has only a 15 percent purging efficiency. In general, loss of labile analytes during trap desorption is a problem that should be addressed to improve the performance of many of the volatile analytes. Although good chromatography was achieved for the volatile amines, the method currently is limited to direct aqueous injection. Further work on the six volatile amines should include pre-analysis concentration method development and investigation of alternate determinative techniques such as ion chromatography, especially for the alcohol amines (2 of the 17 high-interest compounds).

S. V. Lucas, M. Cooke, and T. F. Cole are with Battelle Laboratories, Columbus Division, Columbus, OH 43201-2693.
***James Longbottom** is the EPA Project Officer (see below).*
The complete report, entitled "Evaluation of Methods for Hazardous Chemicals Listed in Appendix D to 40 CFR 122 (Table V)," (Order No. PB 86-136 520/AS; Cost: $16.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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